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(54) **Insect repellents**

(57) An insect repellent for the protection of clothes contains l-carvone. The l-carvone may be present as the compound itself, in varying degrees of purity, or may be present in spearmint oil, of which it forms a main component. It may be mixed with linalool and/or anethol and anti-oxidants may be included. The ingredients are preferably carried on a sublimable substance such as adamantane, endo-trimethylene-norbornane, camphor, cyclododecane or a mixture of two or more thereof. Alternatively the ingredients may be adsorbed n an adsorbent material and enclosed in a vapour permeable sachet.

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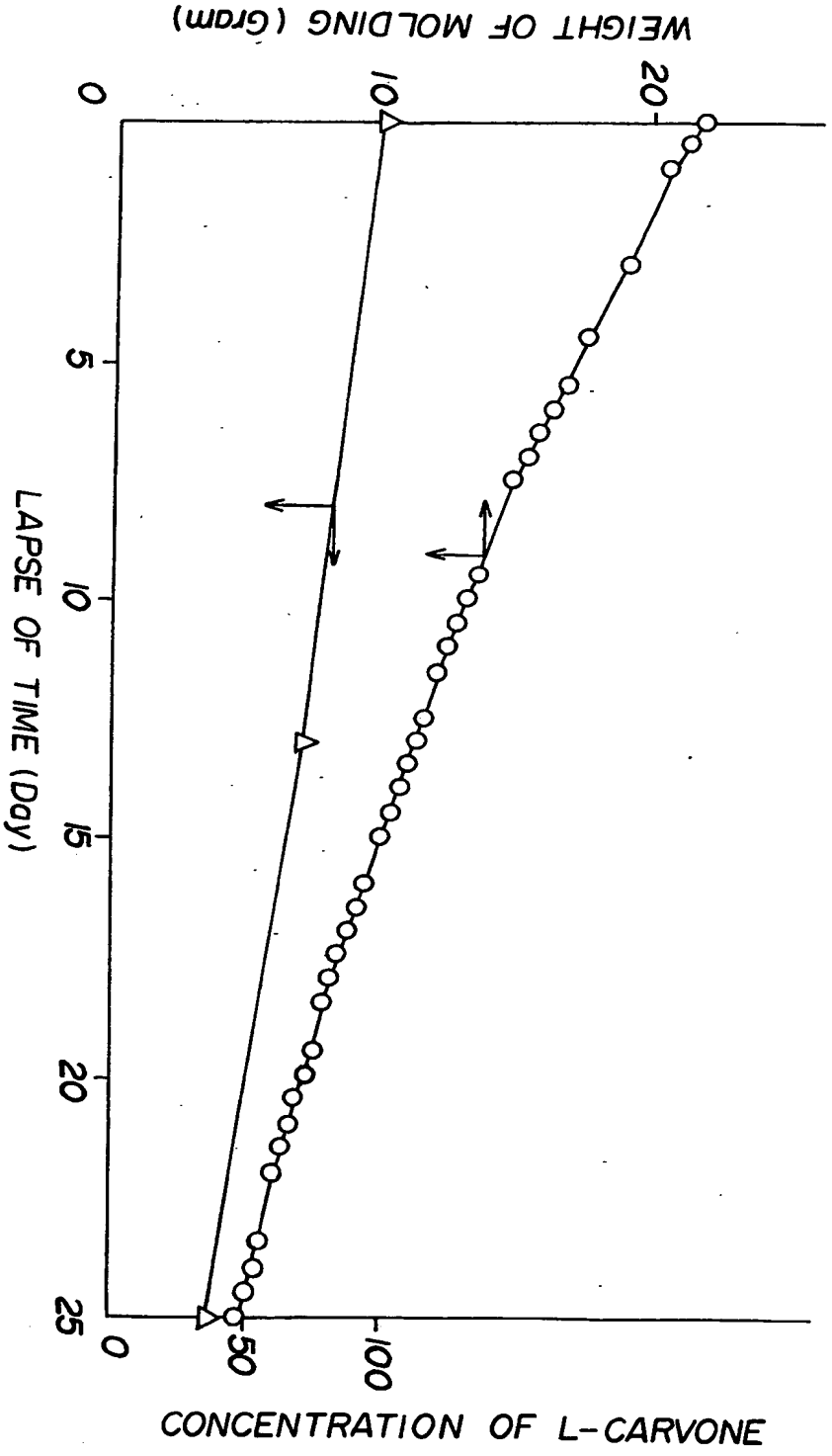

FIG. 1

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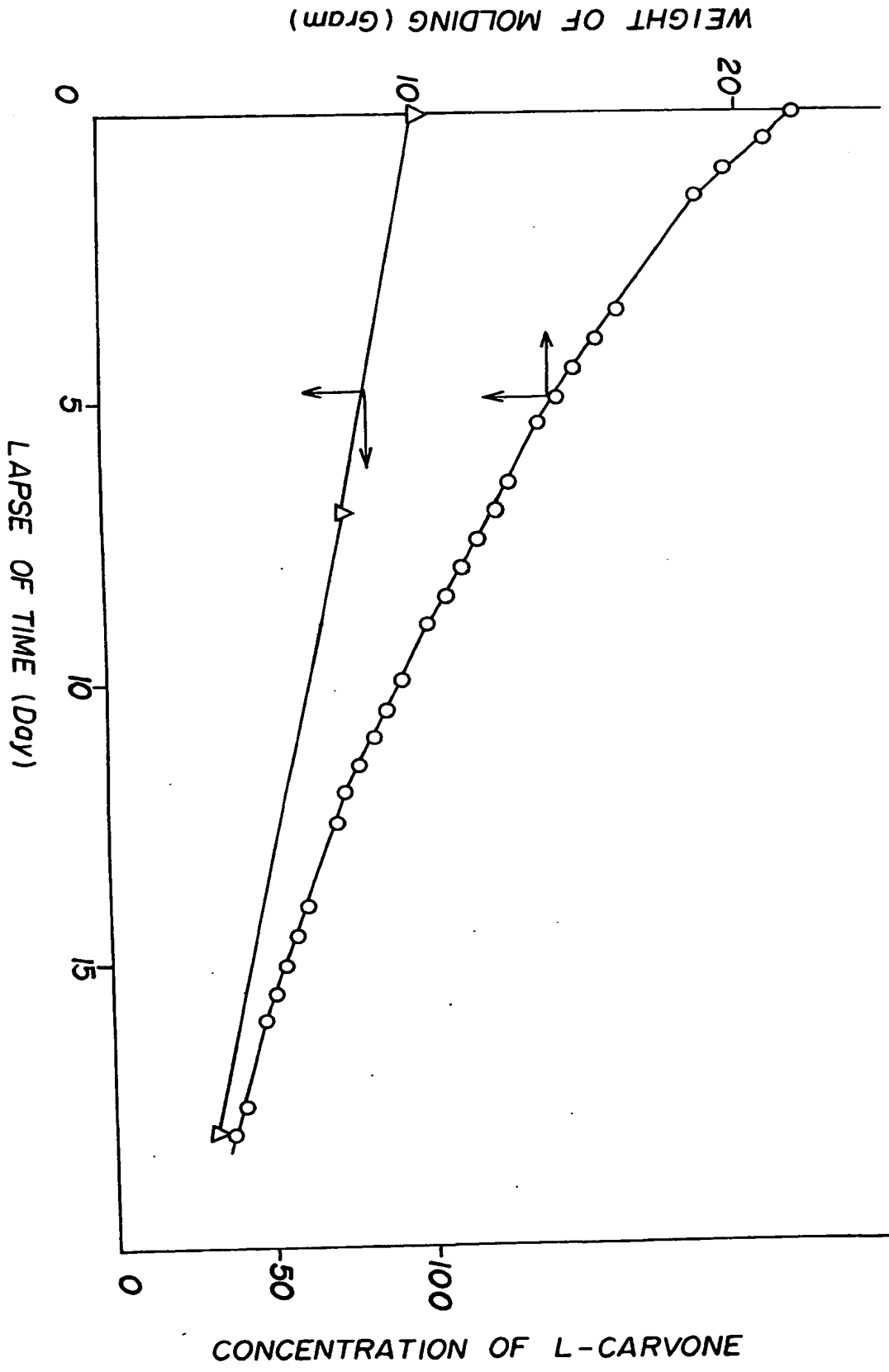

FIG.2

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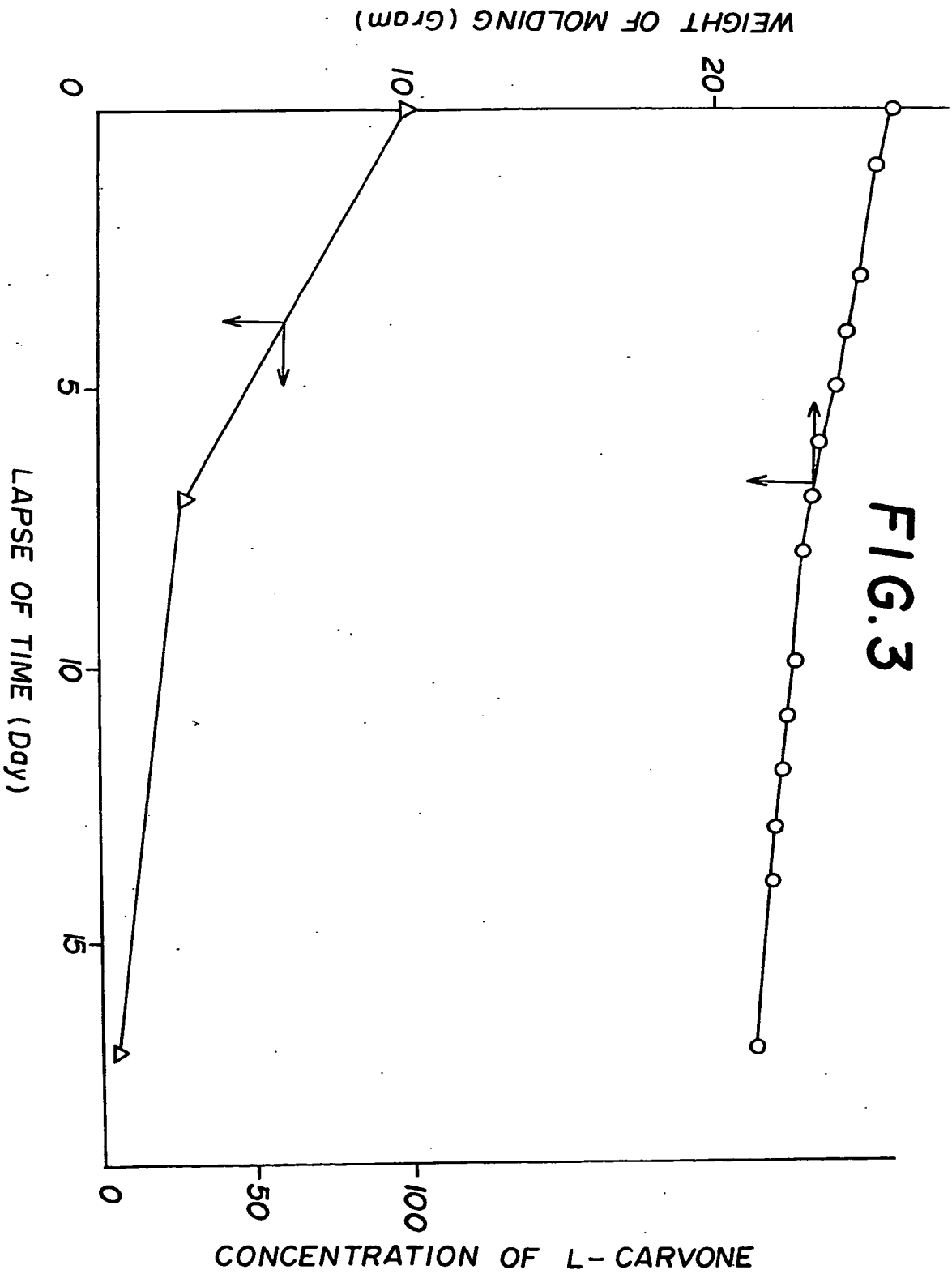


FIG.3

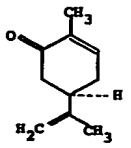
SPECIFICATION

Insect repellents

The invention relates to insect repellents, particularly those intended for the protection of clothes.

Known insect repellents for the protection of clothes include naphthalene, camphor, *p* - dichlorobenzene, aldrin and dieldrin. *p* - Dichlorobenzene is the most widely used, but has relatively strong toxicity and an offensive smell. Aldrin and dieldrin, which are also organic chlorine compounds, are so toxic as to be prohibited in some countries. Naphthalene and camphor are less effective as insect repellents than *p* - dichlorobenzene. A need exists for an effective insect repellent for the protection of clothes which is both non-toxic to humans and inoffensive in smell.

We have found that l - carvone meets this need. l - Carvone is a naturally occurring product, a main component of spearmint oil which is widely used in foodstuffs and in dental care. It has the formula



Accordingly the invention provides an insect repellent containing l - carvone.

The l - carvone may be the pure or substantially pure compound, the crude product of refining, or merely one component of a composition such as a natural refined oil, a mixed spice, a mixed perfume or a mixture of l - carvone and linalool and/or anethole.

The l - carvone may be employed on its own but is usually employed in a mixture with other substances. For example, as it is an oil substance, l - carvone can be employed in the following form: a material such as silica gel, cotton and filter paper is made to absorb and contain a suitable amount of l - carvone and is then packed in a vapour permeable sachet of cloth, Japanese paper or other material. In another embodiment, a sublimable substance such as adamantane, endo - trimethyleneorbornane, camphor, cyclododecane or a mixture of two or more thereof is utilized as a carrier with an insecticidally effective amount of l - carvone. It is possible to add an antioxidant (for example, a quinone, aromatic amine, aldo - amine or phenol) to the insect repellent if desired and/or necessary. In order to prepare a composition comprising a sublimable substance carrier and l - carvone the following methods can be used, that is, the sublimable substance is formed into a suitable shape and is then made to absorb l - carvone, or alternatively both substances are mixed in suitable quantities, and the mixture is then melted by heating and solidified in a suitably shaped mould.

Camph r as the sublimable substances can be mployed alone, but is preferably combined with other sublimable substance such as adamantan so that it can incorporate and retain l - carvone powerfully.

In the manufacture f th ins ct repellent of th invention, the quantity f l - carvon to be employed and the ratio at which it is to be blended with other components can be determined depending upon the intended use and desired effective range of action.

Using insect repellents according to the invention, effective protection can be afforded against insects harmful to clothes. Such insects include the Japanese common hide beetle (attagenus japonicus), cabinet beetle (anthrenus verbasci), case-making clothes moth (tinea pellionella), webbing clothes moth (tineola bisselliella) and carpet moth (trichophage tapetzella). l - carvone is derived from a natural substance and the insect repellent is safe with no toxicity to humans and has an aromatic fragrance. Furthermore, it can also be used as an insecticide because l - carvone kills insects which are harmful to clothes. When l - carvone as an effective component is carried by a sublimable substance, the insect repelling effect can be maintained with a constant strength for a long period of time, that is, the volatilizing speed of the effective component can be kept constant. Moreover, when the effective component is carried by a sublimable substance, the end of the insect repelling effect can be visually judged.

The invention is illustrated by the following Examples, and by the drawings which are graphic representations of the results obtained in Example 12.

Example 1

0.3 g of cotton was soaked in a mixture consisting of 1 g of l - carvone and 5 ml of tetrahydrofuran, and stood for 5 hours at room temperature whereby the tetrahydrofuran evaporated off leaving the cotton impregnated with the l - carvone. The insect repelling properties of this were tested by the following method.

At the middle of a polyvinyl chloride vessel (30 x 21 x 4.5 cm), there was placed a 9 cm diameter, 0.3 cm thick aluminium plate on which 1 g of muslin and the above insect repellent were put. Next, 20 larvae of cabinet beetle (anthrenus verbasci) were put in the vessel. The vessel was covered with a polyvinyl chloride lid (33 x 27 x 6 cm) and placed in a constant temperature and humidity apparatus. The number f insects that encroached upon the above plate in order to eat the muslin was counted every day during a period of 5 days. The lid had a 0.8 cm diameter hole through which the insects could breathe sufficiently.

The number of insects that entered the bait plate and the number of those that died during 5 days are shown in Table 1.

Example 2

Example 1 was repeated except that spearmint il was used instead of l - carvone. The results are shown in Table 1.

Example 3

An insect repellent (4 grams in weight) was prepared by compounding 2 parts by weight f l - carv ne with 100 parts by weight of an 8:2 by weight mixture of endotrimethylene - n rborbane and adamantane. The pr perties of this insect repellent were tested by the method described in Example 1. The results are shown in Tabl 1.

Example 4

Example 3 was repeated except that 4 parts by

weight of spearmint oil was used instead of 2 parts by weight of l - carvone. The r sults are shown in Table 1.

Table 1

Example No.	Number of insects that entered the bait plate*1 1st day	2nd day	3rd day	4th day	5th day	Number of dead insects*2
1	0	0	2	2	2	17
2	0	3	3	3	3	15
3	0	0	3	4	4	14
4	0	4	5	5	5	13

*1 The average of measurements taken five times a day.
*2 The insects did not starve to death because they can survive for more than 7 days even when given no bait.

Example 5

Cotton was impregnated with a solution obtained by dissolving 0.5 ml of linalool and 0.5 ml of l - carvone in 5 ml of tetrahydrofuran, and the tetrahydrofuran was then volatilized off at room temperature. The insect repellent properties of this impregnated cotton were tested by the following method.

A polyvinyl chloride vessel (20 x 50 x 5 cm) was divided into left and right compartments (each 20 x 25 x 5 cm) by a partition plate at the middle of the vessel, and 1 g of muslin (wool) and the impregnated cotton were put in the left compartment. A 1.5 cm diameter hole was bored in the partition plate to provide a passage. Next, ten larvae of 60-day-old Japanese common hide beetles (attagenus japonicus) were put on both sides of the passage. After that, the left compartment was covered with a plastics cover and the right compartment with a wire net, and the insect repelling test was started. The outer air flow was passed from right to left. During the test, the vessel was kept in a constant temperature and humidity apparatus at 30 ± 2°C and at a humidity of 65 ± 3%. The quantity of test cloth (muslin) eaten by the insects during a test period of 7 days was measured. The results are shown in Table 2.

Example 6

Example 5 was repeated except that anethole was used instead of linalool. The results are shown in Table 2.

Example 7

Example 5 was repeated except that spearmint oil was used instead of l - carvone. The results are shown in Table 2.

Examples 8 to 10

Examples 5 to 7 respectively were repeated except that twenty larvae (30-day-old) of the case-making clothes moth (tinea pellionella) were used instead of Japanese common hide beetles (attagenus japonicus). The results are shown in Table 2.

Table 2

	Effective component	Insect	Quantity eaten (mg)
Example 5	l - carvone 0.5 ml Linalool 0.5 ml	Japanese common hide beetle (attagenus Japonicus)	0
Example 6	l - carvone 0.5 ml Anethole 0.5 ml		0
Example 7	Spearmint oil 0.5 ml Linalool 0.5 ml		0
Example 8	l - carvone 0.5 ml Linalool 0.5 ml	Case-making clothes moth (tinea pellionella)	1
Example 9	l - carvone 0.5 ml Anethole 0.5 ml		3
Example 10	Spearmint oil 0.5 ml Linalool 0.5 ml		2

Example 11

100 parts by weight of camphor were melted by heating to 180°C and a predetermined amount f l - carvone was added. Th molten mixtur was

promptly solidified in a test tube by cooling it from the bottom. The test tube containing the solidified mixture was allowed t stand for ne day with its pen end downwards.

The experim nt was repeated using first *p* - dichlorobenzene and then naphthalene instead of camphor. After one day, the presence of absence of liquid flowing down out of the solidified mixture was checked. The results are shown in Table 3. These show the suitabilities of camphor, *p* - dichlorobenzene and naphthalene as carriers for l - carvone. *p*-Dichlorobenzene is clearly least capable of retaining the l - carvone.

Table 3

Sublimable substance 100 parts by weight	l - carvone (parts by weight) 5	10	15	20
Camphor	o	o	o	x
p - dichlorobenzene	o	x	x	x
Naphthalene	o	o	o	x

o: The substance has retaining ability (liquid does not flow down).
x: The substance has no retaining ability (liquid flows down).

Example 12

100 parts by weight of camphor were melted by heating to 180°C and 4 parts by weight of l - carvone were added. The molten mixture was cast into a metal mould (42 mm diameter, 16 mm high) and solidified.

The moulding allowed to sublime by standing it in a stream of air at room temperature, and the change in weight of the moulding and the change in concentration of l - carvone in the moulding were measured. The results are shown in Figure 1. This experiment shows the ability of camphor, the carrier of l - carvone, to retain l - carvone. The concentrations of l - carvone in the moulding are expressed as percentages of the original concentration at the time of moulding.

The experiment was repeated using a mixture consisting of 70 parts by weight of camphor, 20 parts by weight of adamantane and 10 parts by weight of endo - trimethylene - norbornane in place of the camphor. This mixture melted at 160°C. The results are shown in Figure 2.

The experiment was again repeated, this time using naphthalene (melting at 90°C) in place of the camphor. The results are shown in Figure 3.

As may be seen from Figures 1 to 3, naphthalene is much inferior to camphor in its ability to retain l - carvone; it sublimes very slowly and volatilizes l - carvone quickly.

CLAIMS

1. An insect repellent containing l - carvone.
2. An insect repellent according to claim 1 wherein the l - carv ne is present in the form of spearmint oil.
3. An insect repellent according to claim 1 or claim 2 further comprising linalool r anethole.
4. An ins ct repellent according t any preceding claim further comprising an anti-oxidant.
5. An insect repellent according t any preceding claim, wherein th l - carvon and ther ingredients if present are carried by a sublimabl substance.
6. An insect repell nt acc rding to claim 5 wherein the sublimable substance is adamantane, endo - trimethylene - norbornane, camphor, cyclododecan or a mixture of two or mor thereof.
7. An insect repellent according to any of claims 1 to 4 wherein the l - carvone and other ingredients if present are adsorbed on an adsorbent material which is enclosed in a vapour permeable sachet.
8. An insect repellent substantially as described herein with reference to any of the Examples.

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